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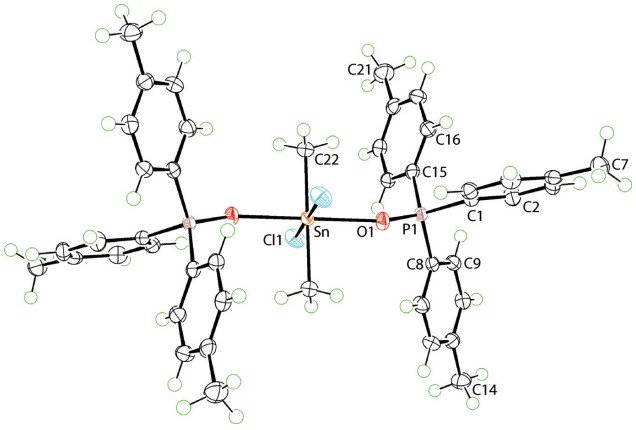
Crystal structure of dichloridodimethylbis(tri-4-tolylphosphane oxide-κ*O*)-tin(IV), $C_{44}H_{48}Cl_2O_2P_2Sn$



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Abstract

$C_{44}H_{48}Cl_2O_2P_2Sn$, orthorhombic, *Pbca* (no. 61), $a = 17.8312(1)$ Å, $b = 12.0291(1)$ Å, $c = 18.5895(1)$ Å, $V = 3987.32(5)$ Å^3, $Z = 4$, $R_{gt}(F) = 0.0196$, $wR_{ref}(F^2) = 0.0564$, $T = 100(2)$ K.

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The molecular structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Source of material

Tri(4-tolyl)phosphine oxide was prepared by the oxidation of tri(4-tolyl)phosphine (Merck) with 30% hydrogen peroxide (Merck) in ethanol. Dimethyltin dichloride (Merck, 0.22 g,

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Table 1: Data collection and handling.

Crystal:	Colourless prism
Size:	0.11 × 0.09 × 0.05 mm
Wavelength:	Cu *Kα* radiation (1.54184 Å)
μ:	7.37 mm^{-1}
Diffractometer, scan mode:	XtaLAB Synergy, ω
θ_{max}, completeness:	67.1°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	47255, 3553, 0.024
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 3391
$N(param)_{refined}$:	235
Programs:	CrysAlis^{PRO} [1], SHELX [2, 3], WinGX/ORTEP [4]

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2).

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
Sn1	0.5	0.5	0.5	0.01216(7)
Cl1	0.55361(2)	0.67812(3)	0.55689(2)	0.02163(10)
P1	0.65744(2)	0.54160(3)	0.38148(2)	0.01201(9)
O1	0.59770(6)	0.48389(9)	0.42508(6)	0.0160(2)
C1	0.68095(8)	0.45559(12)	0.30549(8)	0.0138(3)
C2	0.74054(10)	0.48362(14)	0.26046(9)	0.0186(3)
H2	0.768419	0.549541	0.269227	0.022*
C3	0.75929(9)	0.41574(14)	0.20297(8)	0.0188(3)
H3	0.799884	0.435761	0.172513	0.023*
C4	0.71925(9)	0.31833(13)	0.18929(8)	0.0172(3)
C5	0.65885(9)	0.29248(13)	0.23361(9)	0.0187(3)
H5	0.630181	0.227541	0.224138	0.022*
C6	0.63961(9)	0.35998(13)	0.29159(8)	0.0163(3)
H6	0.598414	0.340793	0.321517	0.020*
C7	0.74249(10)	0.24351(14)	0.12839(9)	0.0227(4)
H7A	0.725930	0.167381	0.138384	0.034*
H7B	0.797212	0.244893	0.123538	0.034*
H7C	0.719477	0.269520	0.083571	0.034*
C8	0.74137(8)	0.56116(13)	0.43352(8)	0.0139(3)
C9	0.79463(9)	0.64230(13)	0.41671(8)	0.0157(3)
H9	0.785775	0.692252	0.378048	0.019*
C10	0.86057(9)	0.65024(13)	0.45636(8)	0.0167(3)
H10	0.896634	0.705307	0.444298	0.020*
C11	0.87430(9)	0.57810(14)	0.51372(9)	0.0175(3)
C12	0.82115(10)	0.49717(13)	0.52984(9)	0.0192(4)
H12	0.830105	0.447167	0.568449	0.023*
C13	0.75509(12)	0.48820(14)	0.49040(9)	0.0179(4)
H13	0.719386	0.432482	0.502176	0.021*
C14	0.94453(9)	0.58833(15)	0.55813(9)	0.0232(4)

Table 2 (continued)

Atom	x	y	z	U_{iso}*/U_{eq}
H14A	0.932651	0.624533	0.603959	0.035*
H14B	0.981554	0.632972	0.531980	0.035*
H14C	0.965122	0.514157	0.567357	0.035*
C15	0.63062(8)	0.67447(12)	0.34630(8)	0.0141(3)
C16	0.60132(9)	0.68328(13)	0.27686(8)	0.0168(3)
H16	0.600004	0.619885	0.246405	0.020*
C17	0.57412(9)	0.78443(14)	0.25226(9)	0.0197(3)
H17	0.553345	0.789359	0.205312	0.024*
C18	0.57689(9)	0.87852(13)	0.29541(9)	0.0186(3)
C19	0.60768(9)	0.86981(13)	0.36417(9)	0.0172(3)
H19	0.610976	0.934087	0.393697	0.021*
C20	0.63349(8)	0.76888(13)	0.39001(8)	0.0158(3)
H20	0.653141	0.763812	0.437398	0.019*
C21	0.54820(11)	0.98855(14)	0.26854(11)	0.0274(4)
H21A[a]	0.554656	1.044997	0.306052	0.041*
H21B[a]	0.576363	1.010491	0.225559	0.041*
H21C[a]	0.494876	0.981855	0.256517	0.041*
H21D[a]	0.529274	0.979899	0.219367	0.041*
H21E[a]	0.507567	1.014404	0.299859	0.041*
H21F[a]	0.589054	1.043040	0.268902	0.041*
C22	0.44035(9)	0.59927(14)	0.42539(9)	0.0186(3)
H22A	0.403899	0.553064	0.399644	0.028*
H22B	0.475561	0.632011	0.390908	0.028*
H22C	0.413961	0.658687	0.451089	0.028*

[a]Occupancy: 0.5.

1.0 mmol) and tri(*p*-tolyl)phosphine oxide (0.64 g, 2.0 mmol) were heated in 95% ethanol (30 mL) for 1 h and filtered. After filtration, the filtrate was evaporated slowly until a white crystalline compound was obtained. Yield: 0.52 g (30.2%). **M. pt.** (Stuart SMP30 digital melting point apparatus; uncorrected): 460–462 K. **IR** (Bruker Vertex 70v FTIR Spectrometer; cm^{-1}): 1598 (m) ν(C=C), 1496 (m) ν(C=C), 1140 (s) ν(P=O), 1083 (s) ν(P-Ar). **^{1}H NMR** (Bruker Ascend 400 MHz NMR spectrometer; $CDCl_3$; ppm relative to Me_4Si): δ 2.21 (s, 6H, CH_3), 2.40 (s, 18H, CH_3), 6.88–7.54 (m, 24H, Ph-H). **^{13}C{^{1}H} NMR** (as for ^{1}H NMR): 21.6 (CH_3), 48.5 (CH_3), 116.9, 129.2, 142.6, 149.9 (Ph—C).

Experimental details

The C-bound H atoms were geometrically placed (C—H = 0.95–0.98 Å) and refined as riding with $U_{iso}(H) = 1.2$–$1.5U_{eq}(C)$. The H atoms of the C21-methyl group were found to be statistically disordered over two positions with one orientation rotated 60° with respect to the other.

Comment

The title compound, $Me_2SnCl_2[O{=}P(4\text{-tolyl})_3]_2$, (I), was investigated in connection with recent structural studies of bis(sulphoxide) [5], bis(triorganophosphane) [6] and bis(triorganoarsane) [7] adducts of R_2SnCl_2. The common feature of the crystallographically determined structures of molecules of the general formula $R_2SnCl_2[O{=}PR'_3]_2$ is the adoption of an all-trans $C_2Cl_2O_2$ coordination geometry for Sn; see ref. [6] for a review. This is also true for the structure of (I), for which the crystal and molecular structures are described herein.

The molecular structure of (I) is shown in the figure (70% displacement ellipsoids; unlabelled atoms are related by the symmetry operation (i) $1-x$, $1-y$, $1-z$). The Sn atom is located on a centre of inversion and is coordinated by symmetry-related pairs of methyl-C [2.1168(15) Å], Cl [2.5735(4) Å] and oxide-O [2.2387(11) Å] atoms. The resulting $C_2Cl_2O_2$ donor set is based on an octahedron with all like-atoms being mutually trans, in accord with expectation [6]. The Sn—O1—P1 angle is bent, at 147.60(7)°.

Very recently, the closely related structure formulated as $(4\text{-}ClC_6H_4)_2SnCl_2[O{=}P(4\text{-tolyl})_3]_2$ was described [6]. As for (I), the Sn atom is situated on a centre on inversion. Reflecting the presence of the electron-withdrawing tin-bound 4-chlorophenyl substituents, the Sn—C [2.1441(15) Å], Sn—Cl [2.5333(4) Å] and Sn—O [2.1746(11) Å] bond lengths have elongated, contracted and contracted, respectively, compared with (I), with, relatively electropositive tin-bound methyl groups.

In the crystal, tolyl-C—H···Cl [C17—H17···Cl1^{ii}: H17···Cl1^{ii} = 2.79 Å, C17···Cl1^{ii} = 3.6779(17) Å with angle at H17 = 157° for (ii) x, $3/2-y$, $-1/2+z$] interactions connect molecules into a supramolecular layer in the *bc*-plane as each molecule participates in four such interactions, i.e. two donor and two acceptor interactions per molecule. The connections between layers to consolidate the three-dimensional architecture are of the type tolyl-methyl-C—H···π(tolyl) [C7—H7c···Cg(C8—C13)^{iii}: H7c···Cg(C8—C13)^{iii} = 2.86 Å with angle at H7c = 154° for (iii) $3/2-x$, $1-y$, $-1/2+z$] and tolyl-phenyl-C—H···π(tolyl) [C19—H19···Cg(C8—C13)^{iv}: H19···Cg(C8—C13)^{iv} = 2.64 Å with angle at H19 = 150° for (iv) $3/2-x$, $1/2+y$, z].

Following standard practices [8] and the program Crystal Explorer 17 [9], the molecular packing in the crystal of (I) was further analysed by calculating the Hirshfeld surface as well as the full and delineated two-dimensional fingerprint plots; there were no significant differences between the disorder models. The main contribution to the surface is due to H···H contacts which account for 68.5% of all contacts with the next most significant contribution being from H···C/C···H contacts, at 19.8%. After this, H···Cl/Cl···H contacts account for 8.6% and C···C contacts amount to 2.9%. These contributions may be compared with those calculated for $(4\text{-}ClC_6H_4)_2SnCl_2[O{=}P(4\text{-tolyl})_3]_2$ [6], i.e. H···H [59.6%], H···C/C···H [22.4%] and H···Cl/Cl···H [15.6%], with the differences correlating with the presence of additional chloride substituents in the latter molecule.

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